Feuer - Cellulose esters.

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CELLULOSE ESTERS

BY

BERTRAM FEUER

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Bertram Feuer

ENTITLED Cellulose Esters

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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CELLULOSE ESTERS

I. Object of work.

The work described in this thesis is an attempt to transform by empirical means, the ordinary motion-picture film into a utilizable product : namely, a lacquer . The writer in order to acquaint himself with the methods of acetylation as used to acetylate cellulose (in the form of cotton) began on a few experiments that will be described later . The results from these first experiments were rather discouraging, hence work was immediately begun on the film . Since the motion-picture film consists of a camphor solution of cellulose nitrate (and probably other ingredients) , it might be well to give a brief historical review that will acquaint the reader with some of the ideas that were with the author in the beginning of this work.

From the time of the discovery by Schönbein of that form of cellulose nitrate called guncotton, to 1851, when pyroxylin was first introduced into photography by Scott Archer,little if any progress had been made in the utilization of pyroxylin in solution, investigators having apparently confined their attention entirely to the development of its use in the solid form. However, the peculiar manner in which pyroxylin is deposited from an ether-alcohol solution and the transparent and resplendent appearance of the resulting film soon drew the attention of experimenters to the possibilities of pyroxylin in solution as a means of producing im-

provements in ~~the~~ various industrial arts; namely, the application of lacquers for textile water-proofing, for protective covering of metals, and for chrome tan leather, leather splits, and flesh splits.

Alexander Parkes, and inventor of great ingenuity, was the first to file a patent for the use of a liquid cellulose nitrate composition as a protective covering and from that time, innumerable patents of this character have been filed.

In order to decrease the inflammability of these pyroxylin lacquers, various processes have been devised. The most interesting of these attempts is that of D. Bachrach (U.S.P. 794581, 1915) who proposes to add to the usual constituents, non aqueous methyl, ethyl, and amyl silicates and similar silicic esters. However, as a free acid is required to be present in order to prevent decomposition of the silicate, it is obvious that the application must be extremely limited.

On the other hand, attempts were made later toward the production of a lacquer from the acetyl derivative of cellulose. Unlike the pyroxylin lacquers, these are uninflammable (both the solvent and the cellulose acetate) and are insoluble and hence immiscible with amyl acetate and amyl alcohol; but the acetyl hydrocelluloses, prepared according to the method of Eichengrün and Becker are soluble in acetone and ethyl acetate, and hence are miscible with pyroxylin lacquers in limited amounts. Cross and Bevan (U.S.P. 804960, 1915) have patented a process for cellulose acetate lacquers employing chloroform as the solvent. Lacquers so produced are transparent, colorless and of an adhesiveness which

compares favorably with that of the nitrates. They are, however, several times more expensive to produce, and for this reason alone have not been used to any extent outside of coating fine copper wires and even for this purpose are no longer used today.

Further attempts to reduce the inflammability of nitrocellulose resulted in the idea of the partial replacement of the nitro by the acetyl groups in the nitrocellulose. Lederer (U.S.P. 1028748, 1912) in his patent based on this idea, treats nitrocellulose with acid chlorides and anhydrides with or without the addition of a condensing agent. The mixed esters so formed are soluble in acetone, burn much more quietly than the nitro-compounds, and can be partially or completely denitrated by suitable saponifying agents. Considering, therefore, the inflammability of the nitro and acetyl derivatives of cellulose it will be noticed that in the case of the mixed ester, a happy medium might be reached.

Let us now consider the nitro-cellulose of the form found in the motion-picture film. It is generally thought that there has been no important utilization of the discarded films, although unsuccessful attempts have been made. The cost of the discarded films is small and the silver recovered from them is sufficient to repay the cost of removal plus the cost of the films. This leaves the recrement, which, so far as is known, has not been utilized.

II. EXPERIMENTS ON THE ACETYLATION OF CELLULOSE (ABSORBENT COTTON)

Note:- In the following the methods are given first and immediately following the observations.

Method No. 1*

Heat ten parts of dry cotton (grease free) with a mixture of 50 parts of acetic anhydride, 2.5 parts of concentrated H_2SO_4 and 150 parts toluene, at a temperature of 70°-80°. As soon as a test portion is soluble in chloroform, the acetylation is complete and the product can be separated off, pressed, washed, and dried. The acetylated cellulose resembles cotton in appearance, but it is brittle and harsh to the touch. It is soluble in chloroform, and acetone and insoluble in water.

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* Worden Technology of Cellulose Esters. Vol. VIII. p.2535 Example 4.

A reflux condenser was used and the temperature kept at 80°C. The cotton dissolved readily. After the reaction took place the mixture turned dark in color. At the end of the acetylation the product was precipitated out of water, filtered off, and dried. The result was a black, brittle product harsh to the touch. The color of the product discouraged further investigation.

Method No. 2*

Soak 100 parts of cotton in dilute H_2SO_4 (cont. 60 per cent H_2SO_4) and then press the cotton until about ten parts of the dilute acid remain in the press cake. Loosen the cotton so treated and introduce into it a mixture of 300 parts of acetic anhydride and 1100 parts of benzene. Shake this frequently for a

period of about 12 hours, and then heat the whole in a reflux apparatus on the water bath at a temperature of from 60°-65° until a test portion is soluble in chloroform. Then press off the acetylated cellulose, remove the excess of acid by means of warm dilute Na_2CO_3 solution, then wash and dry.

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* Worden Technology of Cellulose Esters Vol. VIII, p.2565. Example 5.

This method worked out like Method No. 1 and gave a similar product.

Method No. 3*

Cellulose 10 parts is reacted upon by a mixture of glacial acetic acid 60 parts, acetic anhydride 4 parts H_2SO_4 0.5 part and trioxymethylene 1 part. The cellulose is rapidly attacked losing its texture and forming a very fluid mass with the liquid reagents. After maintaining the mixture at a temperature of about 30° for several hours, 21 parts acetic anhydride are added to complete the acetylation. On subsequent precipitation of the product with water a cellulose acetate is obtained which is soluble in the usual solvents, yielding viscous solutions suitable for making films or substitutes for celluloids.

On addition of the specified amounts of the reacting substances, the mass did not go into solution as described, hence the portions of the reacting substances were doubled. The liquid portion was filtered off by suction and precipitated by pouring into water. The filtrate before being poured into water was of small volume and very viscous. The ppt. finally obtained was white and floculent. After filtering off the water it was dried and the product had the appearance of bread crumbs. The portion

of the cotton that remained, that is did not go into solution was further treated until a partial solution was obtained. This filtrate from the second portion after being precipitated by water remained very finely suspended, probably colloidal, and therefore could not be separated. Several reagents were used to precipitate or salt out of the solution the cellulose acetate of this second portion. The following list shows these used and the results they gave:

$NaOH$ --- no ppt.
HCl --- very slight ppt.
NH_4OH --- slight ppt.
$NaCl$ --- good floculent ppt.
$CuSO_4$ --- good floculent ppt.
Na_2CO_3 --- fine white ppt.
Na_2SO_4 plus $CuSO_4$ --- fine white ppt.

A mixture of $CuSO_4$ and Na_2CO_3 was actually used and the product obtained was primarily the same as that of the first portion except that it was slightly colored by the $CuSO_4$ used.

These products were both found to be insoluble in both acetone and amyl acetate.

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* Chemical Abst. 11, 9, 1301 (1917)

III. ACETYLATION OF MOTION-PICTURE FILMS

1. By refluxing on the water-bath for 12 hours a portion of the film with acetic anhydride and glacial acetic acid in the presence of concentrated H_2SO_4 it was found that a reaction takes place but no product was found by attempting to precipitate in water.

2. By refluxing for 24 hours on the water-bath the same mixture as employed in the first case, only using $ZnCl_2$ as a dehydrating agent, a very viscous solution was obtained. This product was readily precipitated from either water or alcohol. The precipitate was found to be white, opaque, and contained camphor from the original film. It was found to be insoluble in CCl_4, C CH3Cl, Toluene, Xylene, Benzene, Methyl alcohol, ether, acetone, aniline, benzyl alcohol, Iso-butyl alcohol, ethylene bromide, and cold amyl acetate. Hot amyl acetate acted as a solvent and from this solution a thin transparent film was obtained.

3. By allowing a batch of the mixture as made up in the first case and using H_2SO_4(concentrated) as a dehydrating agent to stand at room temperature until the film dissolved and formed a very viscous liquid. This was precipitated from water and gave a product resembling that obtained in the second case. It was later found that the above reaction was greatly hastened by allowing the mixture to stand in the direct sunlight. Acetone and amyl acetate both act as good solvents for this product. The amyl acetate solution when applied to brass gives a water-proof, heat and electric resistance covering. When applied to wood, it forms a very suitable lacquer, very smooth, glossy, transparent and durable.

4. By refluxing on the water-bath a mixture of film and glacial acetic acid no results were obtained.

5. By allowing a mixture of film and acetic anhydride to stand at room temperature a viscous solution was obtained that gave an opaque, horny product soluble in both acetone and amyl acetate when precipitated from water.

6. By allowing a mixture of film, glacial acetic acid, and sulphuric acid to react at room temperature a solution was obtained that gave a white powder, soluble in acetone and insoluble in amyl acetate, by precipitation from water.

7. By allowing a mixture of film, glacial acetic acid, and $ZnCl_2$ to react at room temperature a viscous solution was obtained that gave a product by precipitating from water with properties similar to those of the product mentioned in the fifth case. This product differs from the one of the fifth case in its general appearance; namely, in appearance it is identical with a pure cellulose acetate hydrate.

8. By allowing a mixture of acetic anhydride and concentrated sulphuric acid to react with a portion of film a violent reaction took place. On precipitation from water a black, partly charred product insoluble in both acetone and amyl acetate resulted.

9. By allowing a mixture of acetic anhydride and $ZnCl_2$ to react with some film a reaction takes place similar to that in the fifth case. The product obtained has the properties of that mentioned in the fifth case. Its appearance is different; namely, darker in color and harder.

10. By allowing a mixture of glacial acetic acid,

acetic anhydride, and concentrated sulphuric acid to react at room temperature and then precipitating from water a white, powdery product soluble in acetone and amyl acetate, and insoluble in alcohol (methyl and ethyl) was obtained.

IV. FURTHER EXPERIMENTS WITH MOVING-PICTURE FILMS

1. Attempts were made to combine the film with crude rubber by dissolving the film in molten rubber. The combination took place with a flame. After cooling, the mass became very sticky but rather fluid. The product was found to be soluble in acetone amyl acetate, chloroform, and ether.

2. A portion of film was dissolved in molten rosin. The product obtained after cooling was a hard, brittle, resinous looking substance. It melted at 75°C.±, and was soluble in amyl acetate.

3. It was observed that by treating a portion of film with a mixture of sodium hydroxide and carbon bisulphide no reaction takes place.

4. A portion of film was dissolved in glacial acetic acid and then incorporated with linseed oil. The product was a heavy, dark, sticky substance. Similar results were obtained by dissolving the film first in amyl acetate and then incorporating with linseed (or castor) oil. This product after being properly heated showed good adhesive and drying properties. By heating a longer time a product was formed resembling crude rubber.

5. By treating a portion of film with equal parts of glacial acetic acid and phosphorus oxy-chloride plus a few drops of

concentrated H_2SO_4 a solution was formed that gave an amorphus gray product by precipitation from water. The product is soluble in amyl acetate and forms a powdery substance on the evaporation of the solvent.

6. It was observed that by treating a portion of film with phosphorus oxy-chloride and sulphuric acid and subsequent precipitation from water gave a jelly like product that hardens on drying and is insoluble in amyl acetate.

7. By treating a portion of film with phosphorus oxy-chloride at room temperature and then precipitating from water a product was formed that was insoluble in amyl acetate, acetone, alcohol (ethyl, methyl), and ether.

8. It was observed that the film does not react with or dissolve in a mixture of hydrochloric and formic acids. In this case it was attempted to produce a formic acid ester by treating with formic acid in the presence of nascent hydrochloric acid formed from the reaction of formic acid on calcium chloride.(This was suggested by Dr. H. G. Deming)

9. By dissolving a portion of film in benzoyl chloride and then pouring the solution into a large volume of water,a precipitation was formed. After thorough washing and drying a sodium decomposition test for chlorine was made which gave a positive result. The product was white, opaque, and crumbly.

V. EXPERIMENTS WITH PYROXYLIN

1. A portion of pyroxylin was treated with ferric chloride and hydrochloric acid. The fibrous structure of the pyroxylin was not changed. After thorough washing and drying a chlorine test was made which gave negative results. This suggestion with an attempt to form a chloride ester was given also by Dr. H. G. Deming.

2. By treating a portion of pyroxylin with a solution of sulphur chloride a product was obtained that by analysis showed the presence of sulphur, chlorine, nitrogen. The product was found to be insoluble in amyl acetate, ether, alcohol, and a mixture of ether and alcohol.

3. An attempt to dissolve pyroxylin in molten rosin gave the same results as in the second case under Part lV, page 9. A melting point in this case was not taken,

4. Pyroxylin was dissolved in benzoyl chloride and a product precipitated from water. The excess benzoyl chloride was taken up with Na_2CO_3. At 50° pure benzoyl chloride crystals began to separate out and no trace of the pyroxylin was found.

5. Pyroxylin was allowed to soak in PCl_3 at room temperature for several days. There was no change in structure of the pyroxylin except that it was easily powdered between the fingers. The product was insoluble in alcohol, amyl acetate and slightly soluble in a mixture of ether and alcohol. On analysis a positive test was had for chlorine and a negative one for nitrogen.

VI. THE ACETYLATED FILM

Drawing our attention to the product obtained as described on page 7 under the third case of section III, we find that this product in an amyl acetate solution has the properties of a good lacquer. Applications were tried out on metallic surfaces, plain wood, and stained and varnished woods. The only objection found was its degree of inflammability, nevertheless it has a low degree of uninflammability compared with the ordinary pyroxylin products. The film formed from the lacquer has the following properties:- transparent, colorless, adhesive, resistant to oxidation, water, dilute alkalies, dilute acids, alcohol and ether.

In order to dilute the solvent used in the above mentioned lacquer, experiments were tried using alcohol, ether, CCl_4, acetone, benzol, water glass, and boric acid. Results with these dilutents were difficult to get in most cases, due to the fact that when a certain point is reached in diluting the cellulose is preceipitated out of solution. The only combination that proved successful was diluting with benzol and acetone. The lacquer produced in this way was equal to that produced by using the amyl acetate alone, except that the amyl acetate gave a more lusterous appearance to its product. It was further observed that by the addition of small amounts of Canada balsam much could be added to the adhesiveness and tenacity of the product.

Attention must be drawn to the fact that this lacquer is not similar to what is termed a celluloid lacquer. The so-called celluloid lacquer has the undesirable camphor incorporated

in it which causes the lacquer to become rough and crystalline when applied because the camphor in the dired film evaporates. In our lacquer the camphor is destroyed during acetylation and hence does not affect the resulting product.

VII. CONCLUSION

Due to the limited amount of time for investigation further work can not be done. Nevertheless it might be mentioned that the result of this investigation might lead to the utilization of this product for a "dope" as used for the protective covering of aeroplane wings.

I wish to take this means of expressing my gratitude to Professor Roger Adams, under whose direction this investigation was carried out, for his kindness and advice extended to me during that time.